Works in Progress

DIANA LUTZ

Rhinestone Cowboys

One fills orders for industry, the other conjures rare compounds for their own sake. For both men, crystal growing is an obsessive craft

CALL IT A CALORIE-FREE THANKSgiving. Victor Moritz Goldschmidt, a Norwegian geochemist known as the father of his discipline, owned an islet in a fjord in Norway that was famous for its rare crystals. In 1940, seven years before his death, he gave the islet to the Norwegian Conservation Society. In his deed of gift, Goldschmidt, who was then director of the Geological Museum at the University of Oslo, decreed that all future directors of the museum be allowed exclusive rock-hunting rights on the islet. Whereas another man might have left money for a wake, so that his friends could note his passing with food and drink, Goldschmidt gave his fellows what he knew they would enjoy much more: a feast of crystals.

The fascination with crystals, whether natural or man-made, is not hard to understand: an arrangement of atoms, tamed yet illuminated by their voyage from liquid to solid, emerges in a form that rewards the viewer with scintillating shapes and colors. For investigators who spend their careers making crystals in the laboratory, a romp on Goldschmidt's treasure island would have been the equivalent of an invitation to dinner at Lutèce—an unforgettable event made possible by a benevolent, if absent, host. Surely, few people appreciate an exquisitely prepared meal more than the cooks who toil regularly in their own kitchens.

Scientists who grow crystals in the laboratory savor the experience in the deep, extravagant way that only a Julia Child could understand. The sheer delight of testing new recipes—along with the unplanned successes and frequent duds—gives the work of crystal growers an adventurous, roll-up-your-sleeves quality that both confirms and belies its practitioners' reputation as the blue-collar workers of physics and metallurgy.

At Ames Laboratory, a U.S. Department of Energy institution on the campus of Iowa State University, two such investigators work in separate red-brick buildings. One of them, Thomas A. Lograsso, was trained as a metallurgist and makes a living trying to grow ever-larger crystals of engineering materials, such as a compound of terbium, dysprosium and iron that expands or contracts in a changing magnetic field. The other, Paul C. Canfield, is a physicist who grows exotic compounds, most of them previously unknown, to study their physical properties. Although the two men have worked just three buildings away from each other for more than four years, they are barely acquaintances. Too many cooks, it seems, would spoil the crystal.

Alexandre-Isidore Leroy de Barde, Minerals in Crystallization, *1813*

CRYSTAL GROWING IS ONE OF THOSE accidental occupations, something virtually no child aspires to. Canfield, a slight, brown-haired thirty-six-year-old with an encroaching bald spot and the restless energy of a sparrow, calls crystal growing a kind of no-man's-land between the scientific disciplines, belonging to none and faintly disdained by all. He and his colleagues do what they do to entertain themselves, he quips, and "to keep us fed, to keep the overeducated people off the streets." Scientists who grow crystals are trained as chemists, metallurgists or physicists; they wander into crystal growth on their way to other things. Lograsso, a thoughtful, dark-eyed thirty-nine-year-old who is as slow to speak as Canfield is quick, says he got his Ames job without ever having grown a crystal. Although crystal growth is taught at some universities, the work on the solidification of metals that Lograsso had done as a student at Michigan Technological University in Houghton and as a postdoctoral research associate at Rensselaer Polytechnic Institute in Troy, New York, was as good a qualification as his future employer was likely to find.

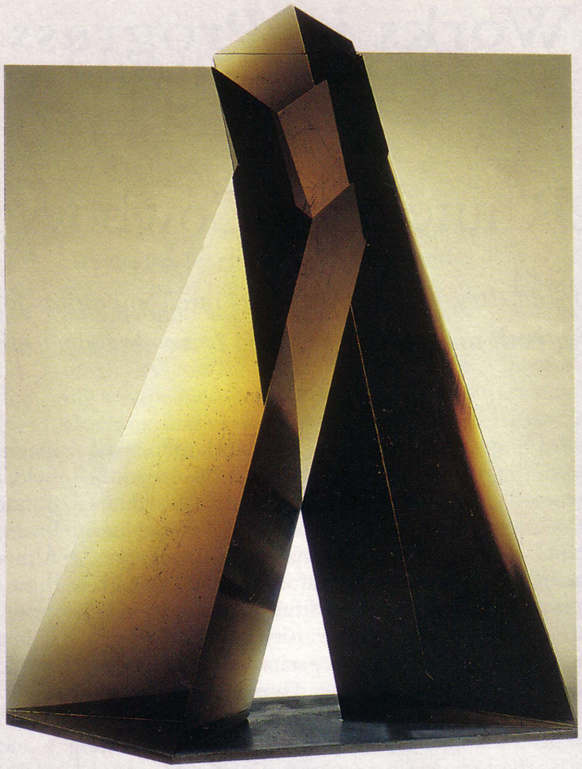
The only kind of crystal growth that gets much attention these days is the growth of silicon and other semiconducting materials for the electronics industry. It is a capital-intensive, high-tech business worth more than $67 billion last year; its practitioners focus on finicky problems of the kind that emerge only after prolonged optimization. But among investigators interested primarily in new materials, the ones that are not yet commodities, crystal growth is to a large extent a skilled craft rather than a true science, pursued with relatively unsophisticated tools.

Asked what crystal making is like, most growers of new materials eventually mention cooking. To be good at crafting crystals one must go to school with one's ingredients, becoming a student of their idiosyncrasies both in isolation and in combination, with only occasional support or guidance from theory. By no large coincidence, Canfield is an accomplished home chef. "After a decade of baking," he wrote in an unpublished essay called "The Cook's Tale," "you get a sense of when nutmeg will help a cake in much the same way that after 2,000 growths you can guess that $YbCu_2Si_2$ [ytterbium-copper-two-silicon-two] will grow out of tin or indium."

Canfield likens the pleasure of showing colleagues his crystals to that of sharing a meal of his own creation. "But a dinner only lasts an evening," he adds, "whereas when I share compounds with my friends, it can last years."

A CRYSTAL IS JUST A TIDY-MINDED SOLid: one in which the atoms are arranged in a regular pattern. Although dozens of special techniques exist for growing bulk crystals, most of them fall into one of two broad categories: growth from solution and growth from the melt. In solution growth, the ingredients of the crystal are dissolved in a solvent; the solution is then cooled or allowed to evaporate until it becomes supersaturated and the excess material crystallizes. It's essentially the technique used to make rock candy.

With the notable exception of quartz, few materials of lapidary or technological interest are soluble in water, so growth from water solution is rarely possible. Instead, solution growth usually demands solvents with high melting temperatures, called fluxes. Rubies, for instance, can be grown from a flux of lead oxide and boron oxide, a process that has the drawback that at the end of the run, the rubies are cloaked in tens of pounds of red-hot flux, which must be gingerly poured or drained from the crucible.



Libenský & Brychtová, Contacts III, *1984–87*

In growth from the melt, by contrast, elements mixed typically in the same proportion as the desired end crystal are melted and then allowed to cool slowly, usually from the bottom of a container up. The process is a lot like the growth of an eave-dangling icicle, only upside down.

In crystal growth, whether from solution or from the melt, the word *slowly* must be taken seriously. Depending on the material and the size of the crystal one wants to grow, the cooling time needed can be weeks, months or even years. Synthetic rubies can be made in a few hours, but synthetic emeralds take a year or longer to grow.

What emerges from the crucible may or may not look like what most of us think of as a crystal. As a general rule, crystals grown from solution are faceted and crystals grown from the melt are not. But a crystal is a crystal, no matter what it looks like. Canfield grows small, faceted crystals from solution (so small—between one cubic millimeter and one cubic centimeter in volume—that his crucibles are generally the size of a thimble). He says he feels sorry for Lograsso, who grows crystals that are larger—between one and ten cubic centimeters—but unfaceted, from the melt. Lograsso, maintains Canfield, "doesn't get to see the beauty." When I repeat that remark to Lograsso, he retorts, "There is an inherent beauty in a single crystal, and even if I can't see its natural habit [the faceted shape it might otherwise have taken], I can see that [beauty]."

One way to understand crystal making is to ask a practitioner how to begin growing a material that has never been grown as a single crystal before. When I put that question to Lograsso, he describes his attempts to grow a family of materials that exhibit a bizarre property called magnetostriction. Ames Laboratory is commissioned to do such work by outside clients—private companies as well as the U.S. Navy and NASA—in what is a typical arrangement for Lograsso.

He grew up on the east side of Detroit, Michigan, the third of five children of a snack-food salesman and a motivating mother who was an administrative assistant for a brewery. Lograsso characterizes his approach to academic and professional problems as pragmatic, a habit of mind in harmony with the craft tradition of crystal growing.

MOVING THROUGH HIS laboratory in a quiet, unassuming way, Lograsso explains that a magnetostrictive material is one that expands or contracts when it is placed in a changing magnetic field. The effect is small: a commercial magnetostrictive alloy has a practically achievable elongation of 1,600 parts per million, which means that a crystal an inch long expands by less than two-thousandths of an inch in the magnetic field. But what matters for engineering purposes is that a signal of one kind can be reliably converted to a readable signal of another kind. A device incorporating a magnetostrictive material can thus change energy from a magnetic form to a mechanical form.

That capability is particularly useful for objects that require precise positioning. One possible future application for Lograsso's research is in NASA's planned Next Generation Space Telescope, which will incorporate a so-called tunable mirror. Behind the mirror, attached to its underside, could be an array of small cryogenic actuators made of a magnetostrictive material. If, say, the mirror warped, its surface position could be fine-tuned by changing the magnetic field of each actuator.

In the 1960s the metallic rare-earth elements terbium and dysprosium were found to exhibit "giant" magnetostriction—magnetostriction about 1,000 times greater than that of any previously known materials—but only at impractically low temperatures. A compound of terbium and iron ($TbFe_2$) that becomes magnetostrictive at room temperature was synthesized in the early 1970s, and dysprosium was later added to it to improve the response of devices to low magnetic fields. The resultant material goes by the unfortunate name Terfenol-D, which makes it sound like a combination lawn fertilizer and weed killer. A crystal of the stuff looks like an ordinary metal rod with a silvery luster.

Lograsso explains that practical devices incorporating magnetostrictive materials are usually made of a single crystal, because the size of the magnetostrictive effect depends on the orientation of the atoms in the crystal. "If you have a device made up of many randomly oriented crystals," he says, "one will contract while the other expands, and the net effect will be zero." What you need instead is a single crystal that is properly oriented to maximize the effect.

MAKING A SINGLE CRYSTAL OF TERfenol-D is a fine example of the crystal grower's art. Indeed, the challenges for the cook arise almost before he begins: there is no good container for the melt. Terbium and dysprosium react with just about anything that contains oxygen, and so the melt cannot be held in the standard crucibles made of quartz, alumina or zirconia.

The secret recipe, says Lograsso, is to grow Terfenol-D without a container, by levitating the hot liquid metal. If that sounds like hocus-pocus, the impression is not far from wrong. Lograsso explains that there are several ways of making liquid metal float in the air, but the most successful method is to let the surface tension of the liquid counterbalance gravity.

To do that, Lograsso takes two polycrystalline rods of Terfenol-D, or rods made up of many crystals of the material. (That, of course, doesn't explain how Lograsso gets the polycrystalline rods in the first place. Suffice it to say there is another method, involving a water-cooled copper hearth, that works best for making Terfenol-D in its polycrystalline form.) Holding the two rods vertically, one above the other with a gap between them, Lograsso heats the gap so that the top of the bottom rod and the bottom of the top rod melt. The melting causes a single droplet to fill the gap between the rods, creating in effect a single rod. The droplet stays in place because of the surface tension of the liquid. As the droplet cools and crystallizes, Lograsso slowly moves a heated coil up the length of the rod (or moves the rod through the coil). In successive small sections, he melts through the existing polycrystalline rod, letting it cool and crystallize as he goes, thereby creating a pencil-size single crystal of Terfenol-D.

Focusing the heat so it melts only a small region of the rod is not easy. The trick is to concentrate the heat so that no more material melts than the surface tension can suspend in space. One way to do that is to induce electrical currents in the rod by varying the current in the coil surrounding it. But there is a catch. Because the energy being added to the rod fluctuates, the molten region can get shaky. When that happens, the liquid metal spills out of the rod, splattering onto the floor of the furnace—the crystal-growing equivalent of a tilt in pinball.

The instability can be quelled by moving the heated coil up the rod faster, much as it is easier to draw a straight line rapidly than it is to draw one slowly. But that strategy invites a new danger. The faster you move the heat source, Lograsso explains, the bumpier the boundary between the liquid and the newly formed solid becomes. The liquid will solidify into dendrites, branching structures like the patterns made by frost on a windowpane. And that's a problem because dendrites tend to form crystals whose orientation is not the strongest for magnetostriction. So with his existing equipment and techniques, Lograsso can make crystals that are good enough, but not perfect. Crystal growth, he reminds me frequently, "isn't all science. Nature still has her hands in it."

IF LOGRASSO IS A CHEF IN A THREE-STAR restaurant, obliging his patrons with special requests, Canfield is a man loose in his own kitchen, flinging sage over his shoulder and dirtying every pan in the cabinet in his quest for something new and tasty. Lograsso grows crystals in a utilitarian spirit, to see what they are good for; Canfield grows crystals in an investigative spirit, to see what they are or even whether they can exist. Unlike Lograsso, Canfield gives his crystals away, to other physicists. Lograsso's crystals, other than the ones made of Terfenol-D, are typically rods the thickness of a broom handle, which he sometimes keeps in manila envelopes in a metal storage cabinet. Canfield's crystals are likely to be small gems, which he stores in Plexiglas boxes between protective sheets of blue plastic foam.

Although his crystals are small, Canfield says they have the simplicity and purity he needs to get a clear picture of the physics of their miniature landscape. For Canfield, making a single crystal is only half the adventure; the other half is measuring its properties. For that reason, he is sometimes considered less a crystal grower than a physicist who grows crystals—or even, as some commercial growers have said dismissively, a physicist who dabbles in intermetallics. (Both scientists, incidentally, are growing crystals that are puny by the standards of the commercial semiconductor industry. Industrial silicon crystals are commonly produced in rods up to a foot long and three inches in diameter. The rod is then sliced into wafers for sale.)

Canfield attributes his crystal-growing bent to his mother, who learned to handle refractory ceramics in her father's denture factory and was also a trained medical technologist. Canfield's father worked for the Congressional Research Service, part of the Library of Congress, and read to his son whatever he happened to be reading himself at the time. The upshot was that while most of his contemporaries were listening to *Winnie-the-Pooh,* Canfield was getting a dose of *Candide.*

He looks for materials that have interesting properties at low temperatures. For example, most metals are good conductors, and as they cool they usually become better conductors. But there is a strange class of metals—one example is vanadium oxide—that suddenly becomes insulating below a critical temperature, an

Libenský & Brychtová, Heart/Red Flower, *1976* anomaly that has long intrigued physicists, including Canfield.

In the world of commerce, crystals have practical applications not only in semiconductors but also in optics, lasers, radiation detectors and jet-engine turbine blades, among other devices. But Canfield freely admits that his crystals generally have no practical applications at all. "This is pure research," he says. Even if he does discover a new material or a new effect, the widget that is ultimately made from that compound will probably use the compound in a polycrystalline form, because single crystals are more difficult and expensive to make.

mation of embryonic crystals), because it's too difficult to do. And usually that limits the size of crystal he can get.

Canfield grows crystals out of a high-temperature flux, a technique not widely used, he says, because it is less predictable than growing from the melt. But flux growth is the ideal tool for a physicist interested in materials because it enables small crystals of many different materials to be grown rapidly, generally in twelve to forty-eight hours. In other words, flux growth is to the physicist much what the telescope was to seafaring explorers: a means of surveying expanses of territory quickly.

THE DIFFERENT LABORATORY equipment used by Lograsso and Canfield point up the contrast in their techniques. Lograsso has roomfuls of hulking furnaces at his disposal: Bridgman furnaces (which employ a crucible that is then pulled from the furnace); Czochralski furnaces (which employ a seed crystal that is placed inside the crucible); and three float-zone furnaces—one induction-heated, one electron-beam and the third optically heated. His latest acquisition is a Czochralski furnace with a video monitor and computer-controlled feedback loops that hold the diameter of the growing crystal constant. Canfield, by comparison, has a half-dozen small box-and-tube furnaces sitting atop surplus metal desks in a basement room that sometimes floods in the spring. But because Canfield grows crystals from solution rather than from the melt, as Lograsso does, he can take on a larger variety of materials.

"The fundamental bifurcation," pronounces Canfield, "is that Lograsso's techniques work only for congruently melting materials or nearly congruently melting materials." A congruently melting material is one that melts all at one temperature, like an ice cube. But many materials are incongruently melting, which means that as the solid is heated, it first forms both a solid of a different atomic arrangement and a liquid; it melts completely only at a higher temperature. The "complex interim region destroys your ability to grow single crystals from the melt," Canfield says, "because it means you have some of the wanted solid and some unwanted solid and it's a big horrible mess."

Most compounds are incongruently melting, and Lograsso can't deal with those by growing crystals from the melt; Canfield, by contrast, can grow congruently and incongruently melting materials with equal ease. The downside is that Canfield, growing crystals from solution, usually doesn't try to control nucleation (the formation of embryonic crystals), because it's too difficult to do.

Libenský & Brychtová, Big Arcus/Arcus III, *1992–93*

MY FAVORITE CANFIELD STORY HAS TO do with an oddball material called cerium-three-bismuth-four-platinum-three ($Ce_3Bi_4Pt_3$, or 343 for short). Canfield cut his teeth on the problem of growing the material, discovered by the physicist Zachary Fisk of Florida State University in Tallahassee, when he was working with Fisk in the early 1990s at Los Alamos National Laboratory in New Mexico.

Three-four-three has interesting physical properties—it belongs to that strange class of metallic materials that become insulating at low temperatures—and it can be grown out of bismuth, one of its constituent elements. Nevertheless, says Canfield, growing it poses many problems: "It's an incongruent melter, it's ternary [made up of three different elements] and it's very finicky. You get small crystals, it nucleates all over the place, the crystals are sort of weedy and inconsequential and, in general, a giant economy-size pain in the ass."

Canfield spent six years trying to grow 343 crystals big enough for inelastic neutron scattering, the measurement that would unlock the material's mysterious electronic and magnetic properties. In the end he began to suspect that the bismuth must be the problem. Molten bismuth is as thick as honey, perhaps too thick for good crystal growth. Even if the solution cooled slowly, atoms emerging from it would not be able to travel far enough to find existing nucleation sites but would instead plate out on whatever was available, creating new nucleation sites and many smaller crystals—useless for Canfield's purposes.

Because Canfield and his colleagues at Ames Laboratory suspected that the bismuth was too thick, they decided to shake up the crucible. Instead of just letting the crucible sit in the furnace and cool slowly over a week or so as they normally might have, they hung it on a wire. Then they attached the wire to a cam shaped like a four-leaf clover. A motor spun the cam, *kachunk, kachunk, kachunk,* bouncing the crucible up and down in the furnace. "And since the crucible was shaken, not stirred," Canfield says, "we called this little mechanism 007, in homage to Ian Fleming. And it worked."

Canfield says he has no desire to grow 343—"my Waterloo"—again. But one discovery has led to another. While he was trying to understand what was wrong with 343 growths, Canfield tried substituting other members of the rare-earth family for cerium and growing 343 out of gallium, lead, tin and antimony, instead of bismuth. One of his discoveries was single-crystal cerium diantimonide.

That crystal is ravishing: shiny, the size of a thumbnail, with scales that peel off like mica. And though so far Canfield has grown it only in thimble-size crucibles, he sees every indication that it could be much bigger: "It loves to grow so much that, as it grows, it will stick out its elbows and shatter crucibles."

So Lograsso, in his laboratory, continues to patiently levitate incipient crystals of Terfenol-D. And Canfield, like a cook sitting down at his own table, radiates deep satisfaction as he considers his samples of cerium diantimonide. "I'm not sure there's any wildly interesting physics to it," he says. "But the crystals are just so exquisitely large and beautiful that, damn it, there should be." •

DIANA LUTZ is an editorial associate of THE SCIENCES *and recently became editor in chief of* MUSE *magazine. She would like to thank Zachary Fisk for an enjoyable evening of conversation about crystal growth and crystal growers.*

THE SCIENCES

NOVEMBER/DECEMBER 1997
VOLUME 37/NUMBER 6

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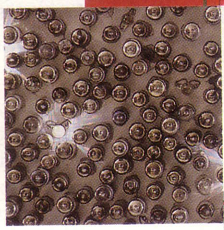

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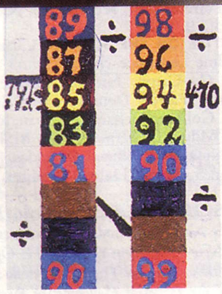

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